Composite materials containing keratin

Field of the invention

The invention relates to the production of improved materials including films, fibres, membranes and the like from keratin protein. The keratin protein is mixed with a polymer, or chemically combined with a polymer or monomer. The invention also provides materials such as films, fibres, membranes and the like made from keratin and polymer.

Background of the invention

Keratins are a class of structural proteins widely represented in biological structures, especially in epithelial tissues of higher vertebrates. Keratins may be divided into two major classes, the soft keratins (occurring in skin and a few other tissues) and the hard keratins (forming the material of nails, claws, hair, horn, feathers and scales).

The toughness and insolubility of hard keratins, which allow them to perform a fundamental structural role in many biological systems, are desirable characteristics found in many of the industrial and consumer materials derived from synthetic polymers. In addition to possessing excellent physical properties, keratin, as a protein, is a polymer with a high degree of chemical functionality and consequently exhibits many properties that synthetic polymers cannot achieve. Keratin is therefore, well suited for use as a base for the development of naturally derived products as an alternative to completely synthetic materials.

Materials in the form of films, membranes coatings and fibers derived from synthetic polymers are commonly used in a wide variety of applications. This is due in large part to the wide range of desirable properties that the materials possess, both in terms of performance in a particular application and processing to create a desired form or shape. The use of materials developed from natural polymers or biopolymers such as cellulose, chitin, chitosan, keratin, alginate, zein and starch is much less extensive (Matsumoto, *et.al.,* J. Appl. Polym. Sci. **60** (1996), 503); (Yang, *et. al.*, ; J. Appl. Polym. Sci. **59**, (1996), 433; Cates, *et. al.*, **21** (1956), 125, Schmpf, *et. al.*, Ind. Eng. Chem. Prod. Res. Dev., **16** (1977), 90). This is due in part to the narrower range of performance properties

natural polymers posses, making them only suitable for certain applications, as well as more limited processing characteristics when compared to synthetic materials It is, therefore, desirable to improve the natural material characteristics through combination and modification.

Hydrolysed keratin has been used as a base for graft coplymerisation (Sastry, T. P., C. Rose, et al. (1997). "Graft copolymerizatiion of feather of feather keratin hyrolyzate : preparation and characteriztion." Journal of Polymer Materials **14**(2): 177-181), however, the nature of a hydrolysate is such that many of the core characteristics of the original protein are lost, and the properties of the resulting modified materials are not as desirable as they could be if the characteristics of the original protein are maintained. This is achieved in the present invention which targets intact proteins as the base for modification. Intimately blended polymer mixtures have been utilised to create materials containing keratin, for example with other biopolymers such as chitin (Tanabe, T; Okitsu, N; Tachibana, A and Yamauchi, K, Biomaterials, 23, 3, 817-825 2002) and synthetic polymers such as polyvinyl alcohol (Kazunori, K., Mikio, S., Toshizumi, T. and Kiyoshi, Y.; J. Appl. Polym. Sci., **91** (2004), 756-762, Sakurada, I; Polyvinyl alcohol fibers; Marcel Dekker: New York, 1985). However, as with previous work on chemical modification of keratin, hydrolysates have been used as the base keratin material. Intact keratin protein fractions are used as the base material in the present invention, a strategy employed to maximise the transfer of desirable characteristics from the keratin source to the final product.

Keratin fibres, such as human hair, wool and other animal fibres, consist of a complex mix of related proteins that are all part of the keratin family. These proteins can be grouped according to their structure and role within the fibre into the following groups:

the intermediate filament proteins (IFP), which are fibrous proteins found mostly in the fibre cortex;

high sulfur proteins (HSP), which are globular proteins found in the matrix of the fibre cortex, as well as in the cuticle.

high glycine-tyrosine proteins (HGTP), found mostly in the fibre cortex.

The ultrastructure of keratin fibres is well known in the art, and discussed in detail by R. C. Marshall, D. F. G. Orwin and J. M. Gillespie, *Structure and Biochemistry of Mammalian Hard Keratin,* Electron Microscopy Reviews, 4, 47,1991. In the prior art described in which keratins are used as a base for chemical modification, the keratin utilized is hydrolysed as one material and no attempt is made to maintain the molecular weight of the protein. Further no attempt is made to fractionate the keratin source into its constituent components. As a result of protein hydrolysis, many of the desirable properties of the proteins are lost. Low molecular weight keratin peptides aggregate with a much lower degree of order to produce materials with much poorer physical properties than the high molecular weight keratins from which they are derived. In addition, irreversible conversion of cysteine as may occur with chemical methods of keratin decomposition, yields a peptide product that has lost the core functionality that that distinguishes it from other protein materials. Particular keratin protein fractions, for example keratin intermediate filament proteins, offer the potential to capture desirable material characteristics for which keratin has been evolved, even further if the proteins are kept intact.

Objection of the invention

The need exists for naturally derived materials that exploit their inherent characteristics and further improve on this through synthetic modification. It is therefore an object of the invention to provide a material, such as a film, fibre, membrane or the like that is made from keratin and a polymer.

Summary of the invention

The invention provides a material comprising an intimate mixture of keratin protein and a water soluble polymer.

The material is preferably a film, membrane or fibre.

The keratin protein is preferably s-sulfonated and is preferably a keratin protein fraction. The keratin protein fraction is most preferably from the intermediate filament protein family.

The keratin protein is preferably intact.

The water soluble polymer may be selected from the group consisting of polyvinyl alcohol, polyvinylpyrolidone and polyethylene glycol.

The invention also provides a method for making material comprising:

a) mixing a keratin protein and a water soluble polymer to form an intimate mixture;
b) casting the aqueous mixture so produced; and
c) drying to create a material.

The invention also provides a method for making a material comprising:

a) mixing a keratin protein and a water soluble polymer to form an intimate mixture;
b) extruding the aqueous mixture produced from step (a) into a coagulation bath through a process of wet spinning.

The physico-mechanical properties of the materials produced may be improved by introducing cross-linker agents to form disulfide bonds and thus remove sulfonate functionalities.

The cross-linking agent used as a reductant is preferably a thiol or thioglycollate salt.

The thioglycollate salt is preferably ammonium thioglycollate solution.

The physico-mechanical properties are preferably wet and dry strength.

The keratin protein mixed with the water soluble polymer is preferably s-sulfonated.

The keratin protein may be a protein fraction and may be from the intermediate filament protein family.

The water soluble polymer may be selected from the group consisting of polyvinyl alcohol, polyvinylpyrolidone and polyethylene glycol.

The invention also provides a method of improving the wet strength properties of the materials produced by the methods of the invention by further incorporating a cross-linking agent into the intimate mixture.

The cross-linking agent is preferably a protein and more preferably is selected from the group consisting of formaldehyde and glutaraldehyde.

The invention also provides a process for improving the mechanical properties of a material produced by a method of the invention by heat treating the composite matrix to enhance its crystalline properties.

The invention also provides a keratin that is chemically linked to a monomer or a polymer material.

The keratin protein is preferably s-sulfonated.

The keratin is preferably a keratin protein fraction and the keratin protein fraction is preferably from the intermediate filament protein family.

The keratin protein is preferably intact.

The monomer or polymer material is preferably from the acrylate, anhydride or epoxide group.

The keratin homopolymer material may be further polymerised.

The invention provides a keratin copolymer material wherein the keratin material produced according to the methods above is further polymerised in the presence of an additional monomer from the acrylate, anhydride or epoxide group.

Within this specification the following definitions are intended:

Unless the context clearly requires otherwise, throughout the description and the claims, the words "comprise", "comprising" and the like, are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense, that is to say, in the sense of "including, but not limited to";

"Material" means any film, fibre, membrane or the like including a sponge block or any matter able to be made or constructed from keratin protein; and

"Intimate" means well blended or mixed together but not chemically linked.

The invention will now be described, by way of example only and with reference to the accompanying Drawings in which:

Figure 1 shows chemically the preparation of keratin protein derivatives;

Figure 2 shows chemically the preparation of a keratin based homopolymer;

Figure 3 shows chemically the preparation of a keratin based copolymer.

Detailed description of the invention

The hard alpha keratin proteins such as those derived from human hair, wool, animal fibres, horns, hooves or other mammalian sources, can be classified into particular components according to their biochemical properties, specifically their molecular weight and amino acid composition. Table 1 illustrates the amino acid composition determined by conventional analytical methods of typical keratin protein fractions known in the art and also the subject of this invention. This involves acid hydrolysis of the analyte which converts all cystine and labile cysteine derivatives to cysteine, typically recorded as half-cysteine.

	SIFP And SIFP - pep	SHSP And SHSP - pep	SPEP	IFP	HSP	HGTP	Whole wool
Cya	0.4	1.7	0.7	0	0	0	0
Asp	7.9	2.6	8	9.6	2.3	3.3	5.9
Glu	15.4	8.6	15	16.9	7.9	0.6	11.1
Ser	10.9	14.3	11.4	8.1	13.2	11.8	10.8
Gly	8.1	9.1	8.4	5.2	6.2	27.6	8.6
His	0.9	0.8	0.9	0.6	0.7	1.1	0.8
Arg	7.9	6.8	6.9	7.9	6.2	5.4	6.2
Thr	6.5	10.4	6.5	4.8	10.2	3.3	6.5
Ala	7.5	3.6	7.5	7.7	2.9	1.5	5.2
Pro	5.4	12.6	5.7	3.3	12.6	5.3	6.6
Tyr	1.1	1.8	1.2	2.7	2.1	15.0	3.8
Val	6.5	6.3	5.8	6.4	5.3	2.1	5.7
Met	0.2	0	0.3	0.6	0	0	0.5
Lan	0.2	0.2	0.3	0	0	0	0
Ile	3.7	2.9	3.4	3.8	2.6	0.2	3
Leu	8.9	3.9	8	10.2	3.4	5.5	7.2
Phe	2.5	1.5	2.1	2	1.6	10.3	2.5
Lys	2.1	0.4	2.1	4.1	0.6	0.4	2.7

Cys	4.2	12.4	4.6	6	22.1	6.0	13.1

Table 1 illustrates an amino acid composition of keratin fractions: S-sulfonated keratin intermediate filament protein (SIFP), peptides derived from S-sulfonated keratin intermediate filament protein (SIFP-pep), S-sulfonated keratin high sulfur protein (SHSP), peptides derived from S-sulfonated keratin high sulfur protein (SHSP-pep), S-sulfonated keratin peptide (SPEP) as used in the invention. Intermediate filament protein (IFP), high sulfur protein (HSP), high glycine-tyrosine protein (HGTP) and whole wool courtesy of *Gillespie and Marshall, Variability in the proteins of wool and hair, Proc. Sixth Int. Wool Text. Res. Conf., Pretoria, 2, 67-77, 1980.* All residues expressed as mol%. S-sulfocysteine, cystine and cysteine are measured as S-carboxymethyl cysteine following reduction and alkylation, and reported as cys.

Table 2 illustrates the molecular weight determined by conventional analytical methods of typical keratin protein fractions known in the art and also the subject of this invention. Conventional analysis involves cleavage of cystine bonds within the keratin using reduction so that the protein mass is determined in its native, uncrosslinked state, most similar to the unkeratinised state of the protein. Mass is determined using polyacrylamide gel electrophoresis. In the case of the peptide SPEP mass is determined using mass spectrometry. Using these methods the keratin is made soluble without any hydrolysis of peptide bonds and an accurate measure of molecular weight is determined.

Keratin protein fraction	Molecular weight/kD
SIFP	40-60
SHSP	10-30
SPEP, SIFP-pep, SHSP-pep	<1
IFP	40-60
HSP	10-30
HGTP	<10

Table 2: Molecular weight of keratin fractions: S-sulfonated keratin intermediate filament protein (SIFP), peptides derived from S-sulfonated keratin intermediate

filament protein (SIFP-pep), S-sulfonated keratin high sulfur protein (SHSP), peptides derived from S-sulfonated keratin high sulfur protein (SHSP-pep), S-sulfonated keratin peptide (SPEP) as used in the invention. Intermediate filament protein (IFP), high sulfur protein (HSP) high glycine-tyrosine protein (HGTP) and whole wool courtesy of *Gillespie and Marshall, Variability in the proteins of wool and hair, Proc. Sixth Int. Wool Text. Res. Conf., Pretoria, 2, 67-77, 1980.*

Both amino acid composition and molecular weight varies across keratin types, between species and also within breeds of one species, for example between wools from different breeds of sheep. The figures given in tables 1 and 2 are indicative for the keratin source stated. However, individual types of keratin proteins, or keratin protein fractions, have distinctive characteristics, particularly molecular weight and amino acid content.

The subject of the invention is materials containing intact S-sulfonated keratin protein fractions. "Intact" refers to proteins that have not been significantly hydrolysed, with hydrolysis being defined as the cleavage of bonds through the addition of water. Gillespie (Biochemistry and physiology of the skin, vol 1, Ed. Goldsmith Oxford University Press, London, 1983, pp475-510) considers "intact" to refer to proteins in the keratinized polymeric state and further refers to polypeptide subunits which complex to form intact keratins in wool and hair. For the purpose of this invention "intact" refers to the polypeptide subunits described by Gillespie. These are equivalent to the keratin proteins in their native form without the disulfide crosslinks formed through the process of keratinisation.

Keratin protein fractions are distinct groups from within the keratin protein family, such as the intermediate filament proteins, the high sulfur proteins or the high glycine-tyrosine proteins well known in the art. Intermediate filament proteins are described in detail by Orwin et al (*Structure and Biochemistry of Mammalian Hard Keratin,* Electron Microscopy Reviews, 4, 47,1991) and also referred to as low sulphur proteins by Gilliespie (Biochemistry and physiology of the skin, vol 1, Ed. Goldsmith Oxford University Press, London, 1983, pp475-510). Key characteristics of this protein family are molecular weight in the range 40 – 60 kD and a cysteine content (measured as half cystine) of around 4%. The high sulfur protein family are also well described by Orwin

and Gillispie in the same publications. This protein family has a large degree of heterogeity but can be characteristed as having a molecular weight in the range 10 – 30 kD and a cysteine content of greater than 10%. The subset of this family, the ultra high sulfur proteins can have a cysteine content of up to 34%. The high glycine-tryosine protein family are also well described by Orwin and Gillespie in the same publications. This family is also referred to as the high tryrosine proteins and has characteristics of a molecular weight less than 10 kD, a tyrosine content typically greater than 10% and a glycine content typically greater than 20%.

For the purpose of this invention a "keratin protein fraction" is a purified form of keratin that contains predominantly, although not entirely, one distinct protein group as described above. In the context of this invention S-Sulfonated keratins have cysteine/cystine present predominantly in the form S-sulfocysteine, commonly known as the Bunte salt. This highly polar group imparts a degree of solubility to proteins. Whilst being stable in solution, the S-sulfo group is a labile cysteine derivative, highly reactive towards thiols, such as cysteine, and other reducing agents. Reaction with reducing agents leads to conversion of the S-sulfo cysteine group back to cysteine. S-sulfo cysteine is chemically different to cysteic acid, although both groups contain the SO_3^- group. Cysteic acid is produced irreversibly by the oxidation of cysteine or cystine and once formed cannot form disulfide crosslinks back to cysteine. S-sulfocysteine is reactive towards cysteine and readily forms disulfide crosslinks.

SIFP can be prepared by methods such as those described in WO03011894.

The broadest feature of the invention includes materials that combine keratin proteins and other polymers or copolymers. Once created the materials are processed into films, membranes, coatings or fibres.

Composite films or membranes are formed from S-sulfonated keratin protein fractions. Intimately mixed solutions of S-sulfonated keratin intermediate filament proteins (SIFP) (for example 5%) and water soluble polymers such as, polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP) (up to 10% solids) are cast and the solution solvents evaporated to leave a keratin-polymer composite film or membrane. The solvent can be

aqueous based and include some percentage of organic based aqueous miscible solven, such as an alcohol.

The physical and mechanical properties of the composite materials can be readily improved through a variety of methods. One method involves treatment with a reducing reagent such as ammonium thioglycolate solution at P^H =7.0 for 1 hour in order to remove the sulfonate functionality from S-sulfonate keratin and introduce cystine disulfides as crosslinks. This causes significant improvement in the mechanical properties particularly wet strength of the films or membranes materials. Conversion is confirmed using Fourier-Transform Infra-Red (FT-IR) spectroscopic studies as the S-sulfonated group gives rise to a strong and sharp absorbance at 1022 cm^{-1} which is observed to disappear on exposure of the S-sulfonated to the reagents described. Another method for the improvement of the physical and mechanical properties of the keratin-co-polymer composites is to increase the hydrogen bonding network between the keratin protein and PVA or PVP using a freezing-thawing process during the constructing composite films or membranes. This is confirmed by the composites insolubility in aqueous solvent, after having been made as an intimate blending keratin protein and polymers from an aqueous solvent (i.e., water).

In addition, the toughness or strength of the keratin based composite films or membrane can be increased by standard protein cross-linking methods including using, typical chemical cross-linkers such as, glutaraldehyde, formaldehyde, carbodiimides, e.g., 1-ethyl-3-(dimethyaminopropyl)carbodiimide, , 2,5-hexanedione, diimidates, e.g., dimethylsuberimidate, or bisacrylamides, e.g., N,N'-methylenebisacrylamide.

Keratin derivatives can be synthesized which involve chemical bonds forming between the keratin proteins and synthetic monomers; such as those from the vinyl family including, acrylates and epoxy acrylates-based monomers (**Figure 1**). As part of the reaction scheme (**Figure 2 and Figure 3**) a polymerisation reaction is initiated between a synthetic monomer and a keratin substance. Graft copolymerization or in-situ graft copolymerization may be promoted by initiating a polymerization process in the presence of the keratin material. The sulphur

containing amino acid residues, prevalent in keratin proteins, act as an initiating site or as a chain transfer or ring-opening reagent and provide a site for the covalent linkage of the synthetic material to keratin proteins. Composite materials formed in this way may then be further processed, either through dry, wet or melt extrusion techniques into films or membranes, fibres and other materials, such as thermoplastic or thermoset materials. These materials can be processed through single or multi extruding or compression molding techniques. The mechanical properties of the synthetic polymer component may be modified by inclusion of suitable co-monomers to allow low-temperature thermoforming processes in which the integrity of the protein component is kept intact.

Composite fibres are prepared through the intimate mixing of a keratin solution with a water soluble polymer, such as PVA or PVP, followed by extrusion into an appropriate coagulation solution in which both components are insoluble. Subsequent strengthening of the composite fibres occurs by introducing a cross-linking reagent, or heat treatment in order to raise the crystallinity of the materials through removal of residual water and the formation of new hydrogen bond between the molecules.

This invention is further illustrated by the following examples which in no way should be construed as being further limiting. The contents of all cited references (including literature references, issued patents, published patent applications, and co-pending patent applications) cited throughout this application are hereby expressly incorporated by reference.

EXAMPLES

Examples 1: PRODUCTION OF COMPOSITE FILMS OR MEMBRANES CONTAINING KERATIN PROTEIN

A 5% S-sulfonated keratin intermediate filament protein (SIFP) solution was prepared using 8.34 gm of wool keratin protein powder (containing 60% solid) dissolved in 100

mL distilled water with 1M NaOH for 2 hours. The P^H was maintained in the range 8.0 – 9.5, and adjusted to 8.5. The keratin protein solution was centrifuged using high speed centrifuging equipment at 27000 g, 12-16°C for 10 mins. A 10% polyvinyl alcohol (PVA) solution was prepared with 100 mL distilled water at 90 °C with stirring. Alternatively, a 10% poly vinylpyrrolidone (PVP) solution was prepared.

A 20 mL SIFP solution was mixed with 6 mL of PVA or 4 mL of PVP solution in a 250 mL beaker, and intimately blended together over 1 hr. The P^H of the blended mixture was 7.8. The blended solution was centrifuged in order to degas. The blended solution was poured into a square petri dish (10 cm x 10 cm x 1 cm) and left in a flat area for 24 hrs to remove solvent under atmospheric conditions. The composite film or membrane was characterized through analysis of mechanical properties such as wet and dry strength using INSTRON tensile testing equipment. Test results are shown in **Table 3**.

Flexibility of keratin films or membranes was increased by incorporating 2% (i.e., 0.2 g per 1.0 gm of keratin protein) of plasticizer(s) such as glycerol or polyethylene glycol (PEG) into the keratin protein solution prior to casting the film or membrane.

Examples 2: PRODUCTION OF CROSS-LINKED COMPOSITE FILMS OR MEMBRANES CONTAINING KERATIN PROTEIN

In order to improve the mechanical properties especially of materials produced as described in **Example 1**, films or membranes were treated with reductants to induce chemical cross-linking. 0.25M ammonium thioglycollate solution at adjusted P^H 7.0 was used to remove the sulfonate group from the S-sulfonated keratin protein, and allow the formation of disulfide bonds (-S-S-).

Examples 3: PRODUCTION OF CHEMICALLY CROSS-LINKED COMPOSITE FILMS OR MEMBRANES CONTAINING KERATIN PROTEIN

Example 3a. An alternative approach to crosslinking was applied to materials prepared according to **Example 1**. 20 mL SIFP solution was mixed with 6 mL of PVA and 4 mL of PVP solution in a 250 mL beaker for 1 hr. The P^H of the blended mixture was 7.8. The blended solution was centrifuged at 27000 g, 12-16°C for 10 mins to degas. 10% - 20% of ethylene glycol diglycidyl ether (EGDE) or glycol diglycidyl ether acrylate (GDEA) was added into the blended solution and stirred for 10 mins. The blended

solution was poured into a square size petri dish (10 cm x 10 cm x 1 cm) and dried at 50 °C for 18 hours.

Example 3b Keratin films were treated with dianhydride cross-linking agents. For example, films prepared by the method outline in example one were immersed at room temperature in a solvent (THF or acetone) solution of BTDA (3,3',4,4' benzophenone tetracarboxylic dianhydride) or PMDA (pyromellitic dianhydride; 1,2,3,4,5 benzenetetracarboxylic dianhydride) (1%). The films were left to soak for a set period of time after which they were removed, washed with a further portion of solvent and allowed to dry.

The resulting chemically cross-linked composite film or membrane was characterized particularly by assessment of the mechanical properties, such as wet and dry strength using INSTRON tensile testing equipment instrument. Test results are shown in **Table 3.**

Examples 4: PREPARATION OF KERATIN PROTEIN DERIVATIVES

42.0 mL (3.0 g keratin solid) of SIFP solution, 6.031 g of glycidal methacrylate (GMA) and 0.6 g of $Na_2S_2O_3$ were loaded in a glass reactor. 20 mL water was added to the reaction mixture with stirring. Reaction temperature was elevated up to 60 °C with continued stirring for 24 hrs. **Figure 1.**

A yellowish white precipitate was obtained after completion of the reaction, which was filtered and repeatedly washed with water to remove excess GMA and reaction catalyst. Filtered product was dried over night under vacuum conditions at 50°C and subsequently freeze-dried for 24hrs. The resulting keratin derivative was characterized using a variety of test, including the *Ninhydrin* test for detecting the absence of amine functionality, and spectroscopic analysis techniques such as FT-IR, ^{1}H-NMR, Solid state NMR and DSC.

Examples 4a: PREPARATION OF KERATIN PROTEIN BASED HOMOPOLYMERS

1.2 g of keratin derivative, prepared as described in example 5, and 0.012 g of AIBN copolymer free radical initiator was added 50 mL of N-methylpyrolidone solvent in a

glass reactor. The reaction was heated to 60 °C with stirring for 24 hrs. (**Figure 2**). The reaction mixture was observed to become highly viscous after 24 hrs. The polymerized product was filtered and dried over night under vacuum condition at 50°C before being re-precipitated into ether, filtered and dried again over night under vacuum conditions at 50°C. The polymerised product was afterward characterized using analytical and spectroscopic techniques such as FT-IR, ^{1}H-NMR, Solid state NMR and DSC.

Examples 4b: PREPARATION OF KERATIN PROTEIN BASED COPOLYMERS

In a variation of Example 4a, various keratin based copolymer materials were synthesized with other vinyl monomers including glycidal methacrylate (GMA), methyl methacrylate (MMA), hydroxyl ethyl methacrylate (HEMA) and acrylic acid (AA) as detailed in Example 4, using similar free radiation initiator (AIBN) and reaction conditions. Copolymers products were purified and characterized as similar, example 4a (in **Figure 3**).

Example 4c In these reactions keratin based co-polymers are synthesised in a solvent system using tin octoate as the catalyst. For example dried keratin SIFP, (3g) was suspended in toluene (100 ml) in a RB flask under a flow of N_2. Lactide (2g) was added and nitrogen purging continued. Tin octoate (45 mg) was added and the temperature of the mixture was raised to 80^{0}C and maintained for 96 hours. The final material was washed extensively with methanol and dried in a vacuum oven. The final material weighed 4.4g, an increase of almost 50%. A similar process can be used for the copolymerisation with caprolactone. The copolymers materials were characterised as previously described.

Examples 5: PRODUCTION OF COPOLYMER FIBERS COANTINING KERATIN PROTEIN

A spinning dope was prepared with SIFP solution, poly(vinyl alcohol), PVA or poly(vinyl pyrrolidone), PVP using a similar method to that described in Example 1, with a variation of concentration in the range 10% -15% and subsequent variation in viscosity for the extrusion of copolymer fibers. Following centrifuging to remove solids

and air bubbles, dope was forced through a spinnerette using a positive displacement pump into a coagulation bath. The coagulation bath had a composition of aqueous sodium sulfate solution and 0.25M ammonium thioglycolate set to pH 6.5. Bath temperature was kept up at 60°C during extrusion of copolymer fibers coatining keratin protein.

Industrial Applicability

The invention provides a film, membrane or fibre material that comprises a mixture of keratin protein and a polymer and that has a wide range of desirable properties over known materials.

The materials may be used as naturally derived alternatives to 100% synthetic polymer materials, for example in the manufacture of consumer and industrial goods. The materials may be further used to bind undesirable agents that are known to interact strongly with proteins, for example heavy metals and biologicals.

Table 3: Mechanical strength (wet and dry strength) of composites containing keratin.

Sample name	**Dry strength (N/m^2) break**	**Wet strength (N/m^2) Break**
KP control	4.2E+07	-
KP (EDGE crosslink)	4.3E+07	8.0E+05
KP/PVA 80:20	3.4E+07	-
KP/PVA 50:50	4.9E+07	-
KP/PVP 80:20	4.95E+07	5.4E+06
KP/PVP (EDGE crosslink)	4.6E+07	7.2E+05
KP/PVA (EDGE crosslink)	4.9E+07	-
KP (thioglycollate crosslink)	1.28E+08	4.88E+06
KP/PMDA/THF		
1wk	8.93E+07	4.44E+06
KP/PMDA/acetone		
2 wk	7.20E+07	5.32E+06
KP/BTDA		
30 sec	3.0E+07	2.6E+05
KP/BTDA		
30 min	6.8E+07	4.9E+05

KP – Keratin protein

EDGE - ethylene glycol diglycidyl ether

PVA – polyvinyl alcohol

PVP – polyvinyl pyrolidone

PMDA - pyromellitic dianhydride; 1,2,3,4,5 benzenetetracarboxylic dianhydride

BTDA - 3,3',4,4' benzophenone tetracarboxylic dianhydride